

Claims

1. A proton-conducting polymer membrane which comprises polyazoles containing phosphonic acid groups and is obtainable by a process comprising the steps
 - A) mixing of one or more aromatic and/or heteroaromatic tetraamino compounds with one or more aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, with at least part of the tetraamino compounds and/or the carboxylic acids comprising at least one phosphonic acid group, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, of which at least part comprises phosphonic acid groups, in polyphosphoric acid to form a solution and/or dispersion,
 - B) heating of the solution and/or dispersion obtainable according to step A) under inert gas at temperatures of up to 350°C to form polyazole polymers,
 - C) application of a layer using the mixture from step A) and/or B) to a support,
 - D) treatment of the membrane formed in step C) until it is self-supporting.
2. The membrane as claimed in claim 1, characterized in that the mixture prepared in step A) comprises aromatic and/or heteroaromatic tetraamino compounds of the formula (A)



where

- Ar is an aromatic or heteroaromatic group,
- Y is a bond or a group having from 1 to 20 carbon atoms,
- p is an integer from 1 to 4 and represents the number of bonds or groups Y via which the group Z is bound to the group Ar,
- r is an integer from 1 to 4 and represents the number of groups Z which are bound to the group Y or, if Y is a bond, to the aromatic or heteroaromatic group Ar, and

Z is a group of the general formula (1)



or the general formula (2)



where R^1 is a hydrogen atom or a group having from 1 to 20 carbon atoms.

3. The membrane as claimed in claim 1 or 2, characterized in that the mixture prepared in step A) comprises aromatic and/or heteroaromatic carboxylic acids of the formula (B)



where

Ar is an aromatic or heteroaromatic group,

X is a halogen atom or a group of the formula OR^2 , where R^2 is a hydrogen atom or a group having from 1 to 20 carbon atoms,

Y is a bond or a group having from 1 to 20 carbon atoms,

p is an integer from 1 to 4 and represents the number of bonds or groups Y via which the group Z is bound to the group Ar,

r is an integer from 1 to 4 and represents the number of groups Z which are bound to the group Y or, if Y is a bond, to the aromatic or heteroaromatic group Ar, and

Z is a group of the general formula (1)



or the general formula (2)



where R^1 is a hydrogen atom or a group having from 1 to 20 carbon atoms.

4. The membrane as claimed in one or more of the preceding claims, characterized in that the mixture prepared in step A) comprises aromatic and/or heteroaromatic tetraamino compounds of the formula (C)



where

Ar is an aromatic or heteroaromatic group,

Y is a bond or a group having from 1 to 20 carbon atoms,

p is an integer from 1 to 4 and represents the number of bonds or groups via which the group Z is bound to the group Ar,

r is an integer from 1 to 4 and represents the number of groups Z which are bound to the group Y or, if Y is a bond, to the aromatic or heteroaromatic group Ar, and

Z' is a group of the general formula (3)



or the general formula (4)



where R^1 is a hydrogen atom or a group having from 1 to 20 carbon atoms.

5. The membrane as claimed in one or more of the preceding claims, characterized in that the mixture prepared in step A) comprises aromatic and/or heteroaromatic carboxylic acids of the formula (D)



where

- Ar is an aromatic or heteroaromatic group which may bear further substituents, for example carboxylic acid groups or derivatives thereof, for example esters or carboxylic halides thereof,
- X is a halogen atom, for example chlorine, iodine or bromine, or a group of the formula OR^2 , where R^2 is a hydrogen atom or a group having from 1 to 20 carbon atoms,
- Y is a bond or a group having from 1 to 20 carbon atoms,
- p is an integer from 1 to 4 and represents the number of bonds or groups Y via which the group Z is bound to the group Ar,
- r is an integer from 1 to 4 and represents the number of groups Z which are bound to the group Y or, if Y is a bond, to the aromatic or heteroaromatic group Ar, and
- Z' is a group of the general formula (3)



or the general formula (4)



where R¹ is a hydrogen atom or a group having from 1 to 20 carbon atoms.

6. The membrane as claimed in claim 1, 3 or 5, characterized in that the mixture prepared in step A) comprises aromatic and/or heteroaromatic tetraamino compounds which contain no phosphonic acid groups and aromatic and/or heteroaromatic carboxylic acids which contain at least one phosphonic acid group.
7. The membrane as claimed in one or more of the preceding claims, characterized in that the mixture prepared in step A) comprises 3,3',4,4'-tetraaminobiphenyl, 2,3,5,6-tetraaminopyridine and 1,2,4,5-tetraaminobenzene.
8. The membrane as claimed in one or more of the preceding claims, characterized in that the mixture prepared in step A) comprises isophthalic acid, terephthalic acid, phthalic acid, 5-hydroxyisophthalic acid, 4-hydroxyisophthalic acid, 2-hydroxyterephthalic acid, 5-aminoisophthalic acid, 5-N,N-dimethylaminoisophthalic acid, 5-N,N-diethylaminoisophthalic acid, 2,5-dihydroxyterephthalic acid, 2,5-dihydroxyisophthalic acid, 2,3-dihydroxyisophthalic acid, 2,3-dihydroxyphthalic acid, 2,4-dihydroxyphthalic acid, 3,4-dihydroxyphthalic acid, 3-fluorophthalic acid, 5-fluoroisophthalic acid, 2-fluoroterephthalic acid, tetrafluorophthalic acid, tetrafluoroisophthalic acid, tetrafluoroterephthalic acid, 1,4-naphthalenedicarboxylic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 2,7-naphthalenedicarboxylic acid, diphenic acid, 1,8-dihydroxynaphthalene-3,6-dicarboxylic acid, bis(4-carboxyphenyl) ether, benzophenone-4,4'-dicarboxylic acid, bis(4-dicarboxyphenyl) sulfone, biphenyl-4,4'-dicarboxylic acid, 4-trifluoromethylphthalic acid, 2,2-bis(4-carboxyphenyl)hexafluoropropane,

4,4'-stilbenedicarboxylic acid, 4-carboxycinnamic acid, or their C1-C20-alkyl esters or C5-C12-aryl esters, or their acid anhydrides or their acid chlorides.

9. The membrane as claimed in one or more of the preceding claims,
characterized in that the mixture prepared in step A) comprises 2,3-diamino-5-carboxyphenylphosphonic acid, 2,3-diamino-6-carboxyphenylphosphonic acid and 3,4-diamino-6-carboxyphenylphosphonic acid.
10. The membrane as claimed in one or more of the preceding claims,
characterized in that the mixture prepared in step A) comprises 2,3-diamino-5-carboxyphenylsulfonic acid, 2,3-diamino-6-carboxyphenylsulfonic acid and 3,4-diamino-6-carboxyphenylsulfonic acid.
11. The membrane as claimed in one or more of the preceding claims,
characterized in that the mixture prepared in step A) comprises aromatic tricarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides or tetracarboxylic acids, their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid halides.
12. The membrane as claimed in claim 11, characterized in that the mixture prepared in step A) comprises 1,3,5-benzenetricarboxylic acid (trimesic acid); 2,4,5-benzenetricarboxylic acid (trimellitic acid); (2-carboxyphenyl)iminodiacetic acid, 3,5,3'-biphenyltricarboxylic acid; 3,5,4'-biphenyltricarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid; naphthalene-1,4,5,8-tetracarboxylic acid, 3,5,3',5'-biphenyltetracarboxylic acid, benzophenonetetracarboxylic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 2,2',3,3'-biphenyltetracarboxylic acid, 1,2,5,6-naphthalenetetracarboxylic acid and/or 1,4,5,8-naphthalenetetracarboxylic acid.
13. The membrane as claimed in claim 11 or 12, characterized in that the content of tricarboxylic acid and/or tetracarboxylic acids is in the range from 0 to 30 mol%, preferably from 0.1 to 20 mol%, in particular from 0.5 to 10 mol%,

based on dicarboxylic acid used.

14. The membrane as claimed in claim 1, characterized in that the mixture prepared in step A) comprises heteroaromatic dicarboxylic acids, tricarboxylic acids and/or tetracarboxylic acids which contain at least one nitrogen, oxygen, sulfur or phosphorus atom in the aromatic.
15. The membrane as claimed in claim 14, characterized in that pyridine-2,5-dicarboxylic acid, pyridine-3,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-2,4-dicarboxylic acid, 4-phenyl-2,5-pyridinedicarboxylic acid, 3,5-pyrazoledicarboxylic acid, 2,6-pyrimidinedicarboxylic acid, 2,5-pyrazinedicarboxylic acid, 2,4,6-pyridinetricarboxylic acid, benzimidazole-5,6-dicarboxylic acid or their C1-C20-alkyl esters or C5-C12-aryl esters or their acid anhydrides or their acid chlorides are used.
16. The membrane as claimed in claim 1, characterized in that the mixture prepared in step A) comprises diaminobenzoic acid and/or its monohydrochloride and dihydrochloride derivatives.
17. The membrane as claimed in one or more of the preceding claims, characterized in that the heating according to step B) is carried out after the formation of a sheet-like structure according to step C).
18. The membrane as claimed in claim 1, characterized in that the solution produced in step A) and/or step B) further comprises dispersed and/or suspended polymer.
19. The membrane as claimed in claim 1, characterized in that the treatment according to step D) is carried out at temperatures in the range from 0°C to 150°C in the presence of moisture.
20. The membrane as claimed in claim 1, characterized in that the treatment of the membrane in step D) is carried out from 10 seconds to 300 hours.

21. The membrane as claimed in claim 1, characterized in that the membrane formed after step D) is crosslinked by action of oxygen.
22. The membrane as claimed in claim 1, characterized in that a layer having a thickness of from 20 to 4000 μm is produced in step C).
23. The membrane as claimed in claim 1, characterized in that the membrane formed after step D) has a thickness of from 15 to 3000 μm .
24. An electrode having a proton-conducting polymer coating which is based on polyazoles and is obtainable by a process comprising the steps
- A) mixing of one or more aromatic and/or heteroaromatic tetraamino compounds with one or more aromatic and/or heteroaromatic carboxylic acids or derivatives thereof which contain at least two acid groups per carboxylic acid monomer, with at least part of the tetraamino compounds and/or the carboxylic acids comprising at least one phosphonic acid group, or mixing of one or more aromatic and/or heteroaromatic diaminocarboxylic acids, of which at least part comprises phosphonic acid groups, in polyphosphoric acid to form a solution and/or dispersion,
- B) heating of the mixture obtainable according to step A) under inert gas at temperatures of up to 350°C to form the polyazole polymer,
- C) application of a layer using the mixture from step A) and/or B) to an electrode,
- D) treatment of the membrane formed in step C) until it has a surface hardness.
25. The electrode as claimed in claim 24, wherein the coating has a thickness of from 2 to 3000 μm .
26. A membrane-electrode unit comprising at least one electrode and at least one membrane as claimed in one or more of claims 1 to 23.
27. A membrane-electrode unit comprising at least one electrode as claimed in claim 24 or 25 and at least one membrane as claimed in one or more of claims 1 to 23.

28. A fuel cell comprising one or more membrane-electrode units as claimed in claim 26 or 27.